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Nickel, ferronickels and nickel alloys — Determination of phosphorus content — Phosphovanadomolybdate spectrophotometric method

Nickel, ferronickels et alliages de nickel — Détermination de la teneur en phosphore — Méthode spectrophotométrique au phosphovanadomolybdate

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 155, *Nickel and nickel alloys*.

This second edition cancels and replaces the first edition (ISO 11400:1992), which has been technically revised. The main changes are as follows:

— the title has been reworded;

— Clause 2 has been updated;

— Clause 3 has been added and the subsequent clauses have been renumbered;

— Clause 4 (the former Clause 3) has been partially reworded;

— in Clause 5 (the former Clause 4): the references of several reagents have been added;

— Clause 6 (the former Clause 5) has been partially reworded, namely 6.1;

— Clause 8 (the former Clause 7) has been partially rearranged regarding the numbering of the paragraphs;

— in 8.4 (the former 7.7), Table 2 has been added;

— 8.5, "Check samples" has replaced 7.8, "Number of determinations";

— the Bibliography has been added.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Nickel, ferronickels and nickel alloys — Determination of phosphorus content — Phosphovanadomolybdate spectrophotometric method

1 Scope

This document specifies a spectrophotometric method for the determination of the phosphorus content in nickel, ferronickels and nickel alloys between 0,000 5 % (by mass) and 0,05 % (by mass).

Arsenic, chromium, hafnium, niobium, silicon, tantalum, titanium and tungsten interfere, but the interferences can be avoided by complexation or volatilization (for chromium). The lowest phosphorus content [0,000 5 % (by mass)] can only be reached in samples with low contents of these interfering elements.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Dissolution of a test portion in a mixture of nitric and hydrochloric acids. Fuming with perchloric acid in a perfluoroalkoxy copolymer (PFA) or polytetrafluoroethylene (PTFE) beaker and removal of chromium as volatile chromylchloride.

Complexation of silicon and refractory elements with hydrofluoric acid.

Conversion of phosphorus to phosphovanadomolybdic acid in a perchloric and nitric acid solution.

After addition of citric acid to complex arsenic, extraction of phosphovanadomolybdic acid with 4-methyl-2-pentanone.

Spectrophotometric measurement at a wavelength of 355 nm.

5 Reagents

During the analysis, unless otherwise specified, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity (see ISO 3696).

Verify by blank tests (see 8.2) that all reagents are free from phosphorus. Lots giving high blank values are unsuitable and should not be used. The blank value should be below 0,000 5 % (by mass), calculated for 1 g of test portion.

5.1 Nitric acid, ρ_{20} approximately 1,41 g/ml.

5.2 Nitric acid solution, 1 + 4.

Carefully add 100 ml of nitric acid (5.1) to 400 ml of water and mix.

5.3 Hydrochloric acid, ρ_{20} approximately 1,19 g/ml.

5.4 Hydrofluoric acid, ρ_{20} approximately 1,14 g/ml.

WARNING — Hydrofluoric acid is extremely irritating and corrosive to skin and mucous membranes, producing severe skin burns which are slow to heal. In the case of contact with skin, wash well with water, apply a topical gel containing 2,5 % (by mass) calcium gluconate, and seek immediate medical treatment.

5.5 Perchloric acid, ρ_{20} approximately 1,67 g/ml.

WARNING — Perchloric acid vapour can cause explosions in the presence of ammonia, nitrous fumes or organic material in general. All evaporations shall be carried out in fume cupboards suitable for use with perchloric acid.

5.6 Citric acid, 500 g/l.

Dissolve 500 g of citric acid monohydrate ($H_8C_6O_7.H_2O$) in water, dilute to 1 000 ml with water and mix.

5.7 4-methyl-2-pentanone (methyl isobutyl ketone).

5.8 Hexaammonium heptamolybdate, 150 g/l.

Dissolve 15 g of hexaammonium heptamolybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}.4H_2O$] with water, dilute to 100 ml with water and mix.

Prepare a fresh solution each day. If high and unstable blank values are recorded, it is possible there is a problem with the reagent used. In such a case, switch to another lot.

5.9 Ammonium metavanadate, 2,5 g/l.

Dissolve 2,5 g of ammonium metavanadate (NH_4VO_3) with water, dilute to 1 000 ml with water and mix.

5.10 Sodium nitrite, 50 g/l.

Dissolve 50 g of sodium nitrite ($NaNO_2$) with water, dilute to 1 000 ml with water and mix.

5.11 Fluoro-boric acid.

Add 75 g of boric acid (H_3BO_3) into 600 ml of hot water in a plastic beaker. Add 50 ml of hydrofluoric acid (5.4), dilute to 1 000 ml with water and stir until the boric acid is dissolved.

Keep the solution in a plastic bottle.

The solution should be gently heated if the boric acid tends to crystallize.

5.12 Phosphorus standard solution, 1 g/l.

Weigh, to the nearest 0,001 g, 4,394 g of potassium dihydrogen phosphate (KH_2PO_4) previously dried to constant mass at 110 °C and cooled in a desiccator. Transfer quantitatively into a 1 000 ml one-mark volumetric flask and dissolve it with water. Dilute to the mark with water and mix.

1 ml of this solution contains 1 mg of phosphorus.

5.13 Phosphorus standard solution, 10 mg/l.

Transfer 10,0 ml of the phosphorus standard solution (5.12) into a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this solution contains 10 µg of phosphorus.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 648 or ISO 1042, as appropriate.

Glassware shall be cleaned with hot hydrochloric acid (5.3) and rinsed with water.

Ordinary laboratory apparatus and the following shall be used.

6.1 Spectrophotometer, capable of measuring absorbance at a wavelength of 355 nm.

Using the slit width recommended by the manufacturer and 4-methyl-2-pentatnone (5.7) as the compensating solution, measure the absorbance of the blank solution (see 8.2) at a wavelength of about 340 nm. Then gradually increase the wavelength until the maximum absorbance is reached (this is generally at a wavelength of 355 nm (see NOTE). Use this wavelength for the determination.

NOTE 355 nm is not the wavelength of the maximum absorption spectrum of the complex. It is not possible to use the maximum point since the 4-methyl-2-pentanone starts to absorb the light at a lower wavelength, where a maximum absorbance value is obtained. 355 nm is selected to give the highest absorption without giving negative absorption values for low concentration due to the absorption of the solvent.

6.2 Perfluoroalkoxy copolymer (PFA) or polytetrafluoroethylene (PTFE) plastic beakers

NOTE The PFA beakers have graphite bases and are specially constructed for fuming of acids up to 280 °C.

Before use, the beakers shall be thoroughly cleaned. Fill the beakers with hydrochloric acid (5.3), diluted 1 + 1, and boil for approximately 2 min. Rinse with water.

7 Sampling and sample preparation

Sampling and preparation of the laboratory sample shall be carried out by normal agreed procedures or, in case of dispute, by appropriate national standards.

The laboratory sample normally is in the form of millings or drillings and no further preparation of the sample is necessary.

If it is suspected that the laboratory sample is contaminated with oil or grease from the milling or drilling process, it shall be cleaned with high purity acetone and then dried in air.

If the laboratory sample contains particles or pieces of widely varying sizes, the test sample should be obtained by riffling.

8 Procedure

8.1 Test portion

Weigh to the nearest 0,001 g a test portion according to the presumed phosphorus content in the sample as shown in Table 1.

Table 1 — Mass of the test portion

Presumed phosphorus content % (by mass)	Mass of the test portion g	Maximum content of the interfering elements [% (by mass)]					
		As	Hf	Nb	Ta	Ti	W
0,000 5 to 0,010	1,0	0,05	0,1	1	0,1	2	2
0,002 0 to 0,040	0,25	0,2	0,5	5	0,5	10	8
0,005 0 to 0,050	0,10	0,5	1,5	10	1	25	25

8.2 Blank test

In parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all reagents as used for the determination, but omitting the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

Transfer the test portion into a plastic beaker (6.2), and add 5 ml of nitric acid (5.1) and 5 ml of hydrochloric acid (5.3). For samples with high contents of niobium, silicon, tantalum, or hafnium, also add 7 ml of hydrofluoric acid (5.4). Fit the beaker with a PTFE cover and heat gently until the reaction ceases. Add 10 ml of perchloric acid (5.5) and, leaving a small opening to release the vapours, evaporate to dense perchloric acid fumes.

NOTE Nickel and some copper-bearing nickel alloys, will dissolve more readily in nitric acid (5.1), diluted 1 + 1.

8.3.2 Removal of chromium

For samples containing more than 0,1 % (by mass) of chromium, continue fuming until no droplets are observed on the cover and all the chromium is oxidized to the hexavalent state. Start adding hydrochloric acid (5.3) drop by drop to the fuming solution in the partly covered beaker, until coloured fumes are no longer liberated. Then restart fuming to reoxidize the remaining chromium. Repeat the treatment until no yellow fumes appear when the hydrochloric acid is added. Cool to room temperature.

8.3.3 Complexation

Add 25 ml of nitric acid solution (5.2) and 4 ml of hydrofluoric acid (5.4) to the test solution, and continue heating for 8 min to 10 min until all the precipitates are dissolved.

It is important that the precipitated refractory oxides dissolve completely. If this does not happen, another 2 ml of hydrofluoric acid (5.4) should be added and the boiling repeated. If the precipitate still remains undissolved, a new test sample of lower mass should be taken for the determination.

Add 10 ml of the sodium nitrite solution (5.10) and continue boiling the solution for 10 min in order to reduce any residual dichromate and to expel all nitrous fumes. Rinse the walls of the beaker a few times with water during boiling.

Add 40 ml of fluoro-boric acid (5.11), rapidly cool the test solution between 20 °C and 30 °C, and proceed immediately with the colour development.

NOTE The oxides can precipitate again if it took more than 10 min to cool the solution.

8.3.4 Colour development and extraction

Add 10 ml of the ammonium metavanadate solution (5.9) and 15 ml of the hexaammonium heptamolybdate solution (5.8) to the cooled clear solution. Allow to stand at a temperature between 18 °C and 25 °C for a minimum of 7 min, but not longer than 15 min.

Transfer the solution into a 250 ml separating funnel which has been marked at 100 ml volume and, if necessary, make up to this mark with water. Add 10 ml of citric acid (5.6), mix, and immediately add 40 ml of 4-methyl-2-pentanone (5.7). Shake the funnel for 30 s. Allow the two layers to separate and discard the lower (aqueous) phase.

Dry the inside of the stem of the separating funnel with a small piece of filter paper. Filter the organic layer through a dry filter paper into a small dry beaker. Proceed immediately with the spectrophotometric measurement.

8.3.5 Spectrophotometric measurement

Ensure that the temperature of the test solution will not vary of more than ± 1 °C.

Carry out the spectrophotometric measurement of the test solution (see 8.3.4) at a wavelength of 355 nm, in 10 mm optical path length cells, against 4-methyl-2-pentanone (5.7) as the reference.

8.4 Establishment of the calibration curve

Transfer the volumes of the phosphorus standard solution (5.13) shown in Table 2 into a series of plastic beakers (6.2) and proceed as specified in 8.3, while omitting the step described in 8.3.2.

Subtract the absorbance of the zero member from the absorbance values of each of the other calibration solutions.

Plot the net absorbances against the mass, in milligrams, of phosphorus added.

Table 2 — Calibration solutions

		Phosphorus contents in the test portion (%, by mass)		
Phosphorus standard solution (5.13) (ml)	**Corresponding phosphorus mass** (mg)	**Test portion** (1 000 mg)	**Test portion** (250 mg)	**Test portion** (100 mg)
0	0	0	0	0
0,5	0,005	0,000 5	0,002	0,005
1,0	0,010	0,001 0	0,004	0,010
2,0	0,020	0,002 0	0,008	0,020
4,0	0,040	0,004 0	0,016	0,040
6,0	0,060	0,006 0	0,024	0,060
8,0	0,080	0,008 0	0,032	0,080
10,0	0,100	0,010 0	0,040	0,100

8.5 Check test

The performances of the method may be checked by analysing, in parallel with the determination and following the same procedure, one or more samples of the same alloy grade whose phosphorus content is known.

9 Expression of results

9.1 Calculation

Correct the absorbance reading of the test solution (see 8.3.5) by subtracting the absorbance reading of the blank test (see 8.2). Convert the net absorbance of the test solution in milligrams of phosphorus by means of the calibration graph (see 8.4).

The phosphorus content, w_P, expressed as a percentage by mass, is given by Formula (1):

$$w_P = \frac{m_2}{10.\, m_1} \tag{1}$$

where

m_1 is the mass, in grams, of the test portion;

m_2 is the mass, in milligrams, of phosphorus found in the test portion.

9.2 Precision

9.2.1 Laboratory tests

Up to eight laboratories in six countries participated in the testing of this procedure on two nickel and four ferronickel samples (seven laboratories in four countries), and on six nickel alloys (eight laboratories in six countries). The samples were analysed three or four times on different days. The nominal composition of the samples is given in Table 3.

Table 3 — Nominal composition of the test samples [% (by mass)]

Nickel and ferronickel						
Sample	**P**	**As**	**Cr**	**Fe**	**Si**	**Ni**
Ni No.1	0,000 05	—	—	< 0,01	—	Remainder
Ni No.2	0,000 8	—	—	0,2	—	Remainder
Fe-Ni No.1	0,01	< 0,001	0,5	Remainder	0,5	25
Fe-Ni No.2	0,01	0,1	4,5	Remainder	5	25
Fe-Ni No.3	0,045	< 0,001	0,5	Remainder	0,6	25
Fe-Ni No.4	0,045	0,1	4,5	Remainder	5	25

Nickel alloys									
Sample	**P**	**Co**	**Cr**	**Cu**	**Fe**	**Mo**	**Ni**	**Nb**	**W**
4D-7	0,01	—	—	32	1	—	65	—	—
4D-8	0,01	—	21	—	4	9	62	3	—
4D-9	0,02	—	18	—	19	3	53	5	—
4D-10	0,02	—	20	—	46	—	31	—	—
4D-11	0,01	1	21	—	20	8	47	—	—
4D-12	0,005	42	21	—	2	4	20	4	4

9.2.2 Statistical analysis

Results from the interlaboratory test programme were evaluated in accordance with ISO 5725:1986[1)]. The data were tested for statistical outliers by the Cochran and Dixon tests described in ISO 5725:1986.

The principle of the Cochran test is that a set of results is an outlier if the within-laboratory variance is too large in relation to the others. Dixon's test is to determine if the mean from a laboratory is too far from the other laboratory means. Both tests were applied at the 95 % confidence level.

Repeatability and reproducibility were also calculated in accordance with ISO 5725:1986 at the 95 % confidence level. The results of this assessment are given in Table 4.

The phosphorus content in sample Ni No.1 was below the scope of the method and no meaningful results were obtained.

NOTE 1 For sample Ni No.2, one laboratory was rejected as a Cochran outlier.

NOTE 2 For sample Fe-Ni No.4, one laboratory was rejected as a Cochran outlier.

NOTE 3 For sample 4D-12, one laboratory was rejected as a Cochran outlier. When applying the Dixon test, one laboratory was rejected as an outlier for sample 4D-9 and another for sample 4D-10.

Table 4 — Results of statistical evaluation [% (by mass)]

Sample	Mean	Within laboratory standard deviation	Between laboratory standard deviation	Repeatability	Reproducibility
Ni No.2	0,000 91	0,000 07	0,000 12	0,000 2	0,000 4
Fe-Ni No.1	0,010 1	0,000 4	0,000 2	0,001 2	0,001 4
Fe-Ni No.2	0,010 0	0,000 4	Not available	0,001 2	Not available
Fe-Ni No.3	0,043 7	0,001 4	0,002 1	0,003 8	0,006 8
Fe-Ni No.4	0,042 5	0,001 0	0,001 0	0,002 7	0,003 8
4D-7	0,012 0	0,000 6	0,000 7	0,001 6	0,002 6
4D-8	0,008 9	0,000 9	0,001 5	0,002 4	0,005 0
4D-9	0,014 8	0,000 8	0,000 6	0,002 3	0,002 8
4D-10	0,018 5	0,000 3	0,000 7	0,001 0	0,002 2
4D-11	0,013 5	0,000 6	0,000 8	0,001 6	0,002 7
4D-12[a]	0,005 4	0,000 1	0,000 8	0,000 4	0,002 2

[a] Certified reference material BAM 328-1, having a phosphorus certified value of 0,005 %, by mass.

10 Test report

The test report shall include the following information:

a) the method used by reference to this document, i.e. ISO 11400;

b) all information necessary for the identification of the sample, the laboratory, and the date of analysis or of the test report;

c) results and the units in which they are expressed;

d) any unusual characteristics noted during the determination;

e) any operation not specified in this document or any operation that could have influenced the results;

1) Cancelled and replaced by the ISO 5725 series.